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# Using Very Small-scale Experiments to Investigate Materials: The 21st Century Direction in Basic Pu Research?

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# **Using very small-scale experiments to investigate materials: The 21st Century direction in basic Pu research?**

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## *Abstract*

Reseachers at Lawrence Livermore National Laboratory have developed several techniques to probe the properties of Plutonium using tiny microgram-to-milligram samples. This commentary describes the advantages of this experimental approach, and contains examples of successful experimental setups. One motivation for such experiments is that they couple well to computational simulations of electronic and atomistic properties and processes, and examples of this coupling are discussed.

## **Introduction**

In recent years, several instruments and capabilities have become available that make experiments at the “very small scale” significantly more accessible. One such instrument is the *in house* Transmission Electron Microscope (TEM) that has sophisticated vacuum transfer holders and is capable of spectroscopic investigations. An important capability is the availability of high intensity x-ray synchrotron sources that allow relatively high-collection rate studies of small actinide samples. Coupled with the development of techniques to process and characterize such samples, Pu experiments at the “very small scale” are significantly more practicable. In this commentary, I review the arguments for using such experiments and present several examples.

## **Why very small scale experiments?**

What are very small scale experiments? In the context of this article,

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I mean the class of experiments that utilize samples weighing micrograms to milligrams. Examples include diamond anvil experiments that have typical radii of less than 100 micrometers and thickness of approximately 10's of micrometers and thus weigh several micrograms. Such sample sizes translate into reduced health hazards from accidental exposure and reduced security risks associated with larger samples. For this reason the handling requirements are greatly reduced and the cost of each experiment is significantly lower than if the samples weighed a gram or more.

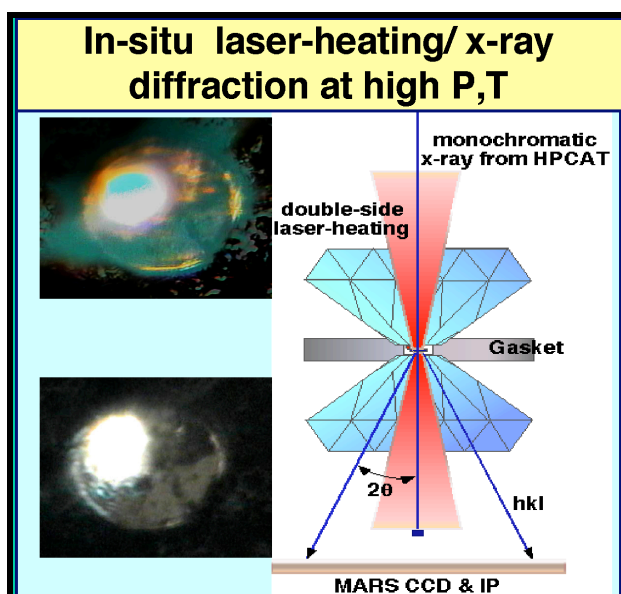


Figure 1

An example of a diamond anvil cell with a very small sample. [1]

From the perspective of a program manager, the reduced costs result in more experiments. From the perspective of the scientific investigator, certainly more experiments are advantageous. But perhaps the most important advantage is that these very small-scale samples can be used to access types of experiments that probe atomic scale phenomena in single crystalline regimes of polycrystalline samples. Additionally, in diamond anvil cells, they can be used to access a greater range of pressure-temperature-density phase space for studies of equations of state and transport properties.



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### **Handling very small scale (VSS) Pu samples**

To reduce costs, tiny Pu samples are transferred out of the main Pu facility at the earliest opportunity. They then are processed in a facility called the Micro Plutonium Laboratory, in a less secure area. This laboratory further fabricates individual samples in glove boxes and encapsulates them inside sealed holders. [2] Samples taken from the same starting material are then characterized in a nearby transmission electron microscope. [3] And if they are to be used at remote locations, the encapsulated sample is then sealed in a special shipping container. There is a significant amount of art and innovation involved in developing both the sample preparation tools and the experimental techniques to probe such samples.

### **New experimental techniques for VSS Pu samples**

LLNL is pursuing several types of VSS Pu experiments. These can be divided into experiments employing on-site facilities such as the TEM and the Physical Properties Measurement Laboratory and experiments sent to off-site facilities such as Advanced Photon Source (APS) and Advanced Light Source (ALS), which are synchrotron-radiation sources.



Figure 2  
The Advanced Photon Source (APS) is a 7 GeV ring located at Argonne Natl. Lab. in Chicago, IL. The Advanced Light Source (ALS) is a 1.5 GeV ring at Lawrence Berkeley National Laboratory in Berkeley, CA.

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### TEM-based experiments

An example of a Pu experiment that utilizes TEM technology is presented in the article in this volume by Adam Schwartz, et al. [4] This article demonstrates that the TEM characterization itself can bring insight to important processes. Using TEM, Schwartz and co-workers have characterized the number and size of He microbubbles accumulating in aged Pu as a function of time.

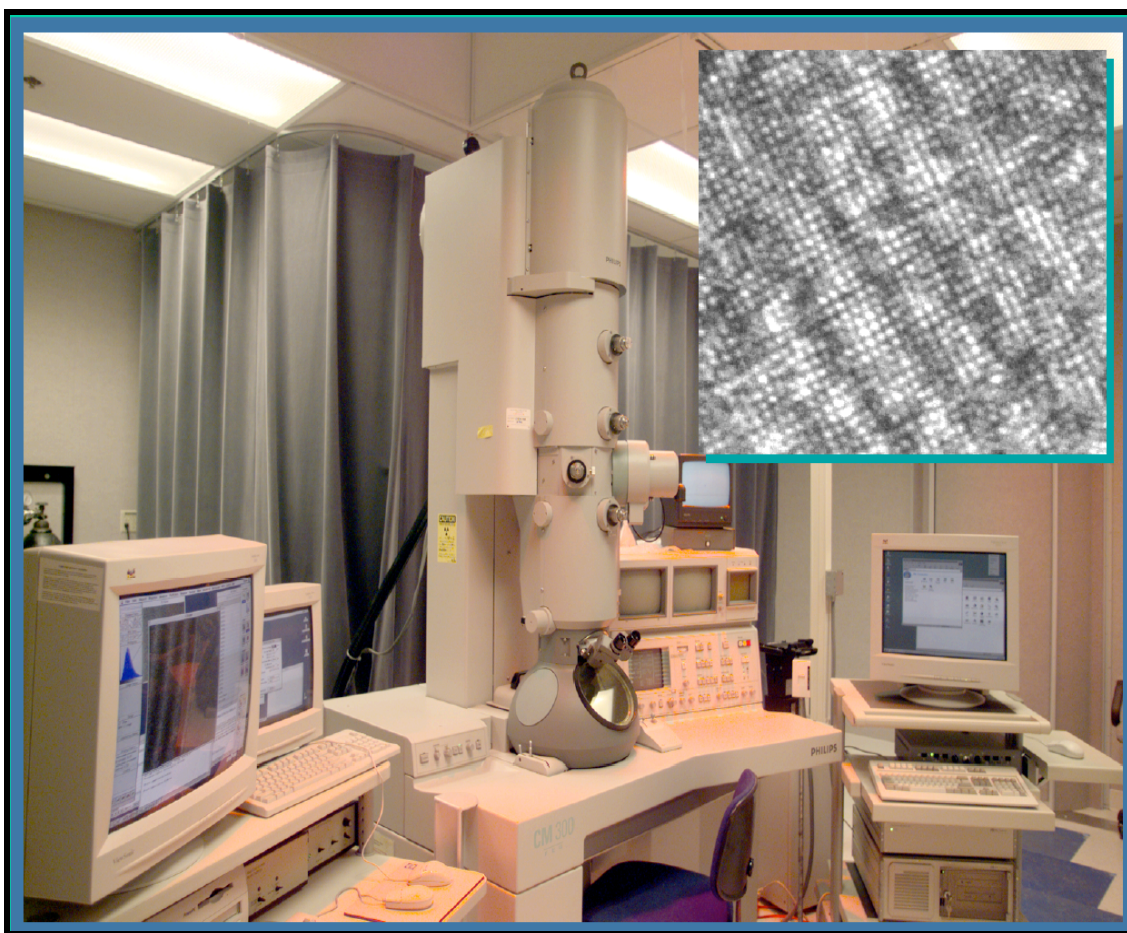


Figure 3

Transmission Electron Microscope (TEM) Facility in the Chemistry and Material Science complex at LLNL. A textured micrograph is shown in the inset.

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This TEM combines capabilities for microscopic imaging, diffraction and spectroscopic analysis via Electron Energy Loss Spectroscopy (EELS). In the case of Pu, these capabilities have been applied to achieve a novel result: measurement of the electronic structure of Pu in a phase specific fashion. [5,6] The nano-focusing of the TEM permits the spectroscopic interrogation of small single crystalline of samples in an otherwise polycrystalline sample. The single crystalline nature of these sections can be confirmed directly with electron diffraction. Examples of this type of study are shown in Figure 4.

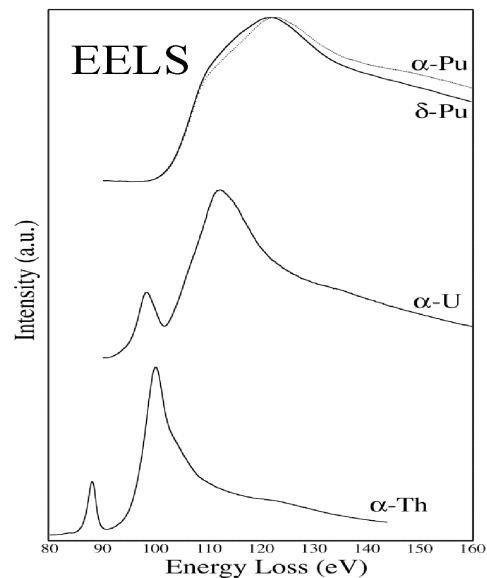
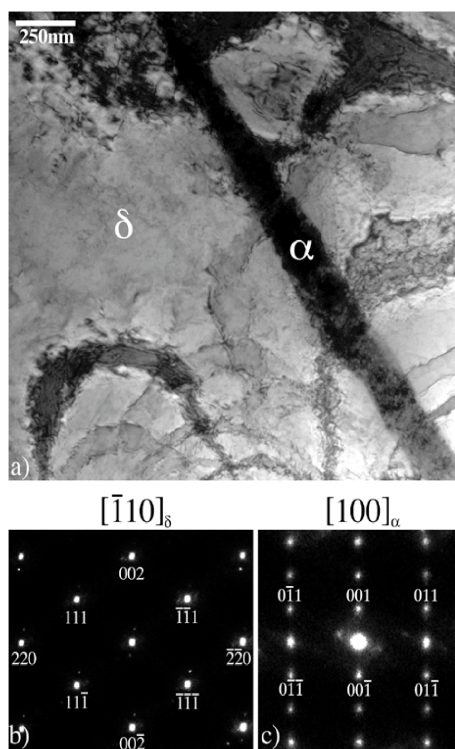


Figure 4  
Micrography and diffraction of Pu  
(to the left) and EELS of Th, U  
and Pu. [5]

TEM-Microscopy and HE-EELS

Below, I will describe how synchrotron radiation experiments are coupled to TEM based investigations.

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### Physical Properties Measurement Laboratory

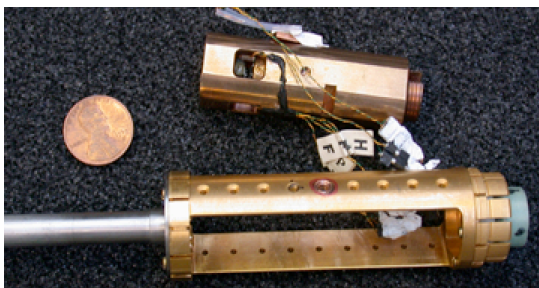


Figure 5a  
Prototype of miniature DAC for high field and low temperature physical property measurements.

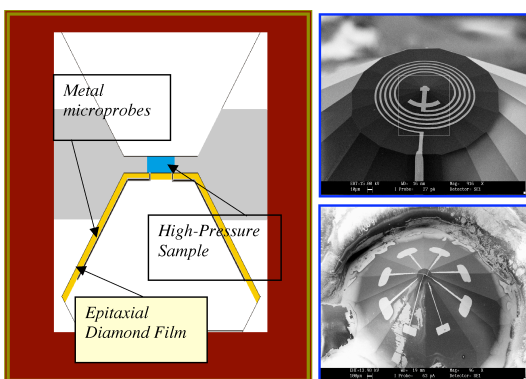


Figure 5b  
Designer DAC diamonds with coil for magnetic studies (top) and point contacts for multipoint resistance and Hall coefficient measurements (bottom).

Michael Fluss, et al in this volume describe measurements to study low temperature behavior of the magnetic susceptibility by tuning the specimen systematically through chemistry, magnetic field, and pressure variations. A special example of tuning is to allow the specimen to accumulate radiation damage, at cryogenic temperatures, caused by spontaneous alpha decay. Future pressure studies by this group of researchers will employ a new type of diamond anvil cell. This cell is an example of so-called “designer diamond anvils” being developed by S. Weir of LLNL and Y. Vorha at U. Alabama. [8] Such cells employ tiny printed circuits embedded in epitaxially-deposited diamond on one of the two diamond coulets; the circuits can be designed to act either as magnetic coils (as in the Fluss experiment) or as leads to ohmically heat the sample or to measure electrical



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resistance. (See Fig. 5). Miniaturizing the diamond anvil cell will allow it to be employed in a Physical Properties Measurement System where the specimens can be exposed to magnetic fields of 16 Tesla and temperatures as low as 2K. Hence both pressure and magnetic field will be simultaneous experimental variables in these experiments.



Figure 6a  
The physical properties measurement system with attachments for magnetic and resistive property measurements shown.

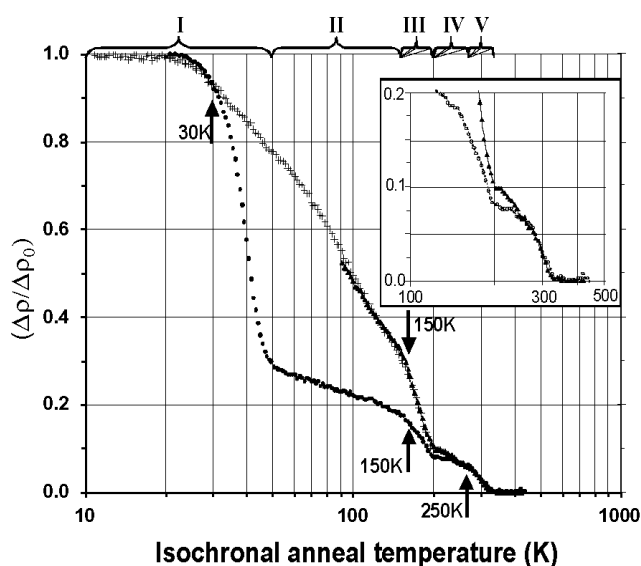


Figure 6b  
The Physical Properties Measurement Laboratory provides a suite of analytical capabilities to pursue studies of actinide properties. To the left is shown resistivity measurements of  $\delta$ -Pu (Ga) under isochronal annealing conditions. [9]

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### Synchrotron Radiation based Experiments

An example of VSS Pu experiments utilizing synchrotron radiation is presented in this volume by James Tobin et al. [10] In his experiment, x-ray absorption spectroscopy (XAS), photoelectron spectroscopy (PES) and Resonant Photoelectron Spectroscopy (RESPES) are applied to Pu to probe the 5f electrons in actinides. The x-rays in this experiment are produced by the Advanced Light Source mentioned earlier. The results of the XAS study have been used in conjunction with the EELS work, to provide a confirmation that High Energy-EELS (HE-EELS) is equivalent to XAS under these conditions [5,6]

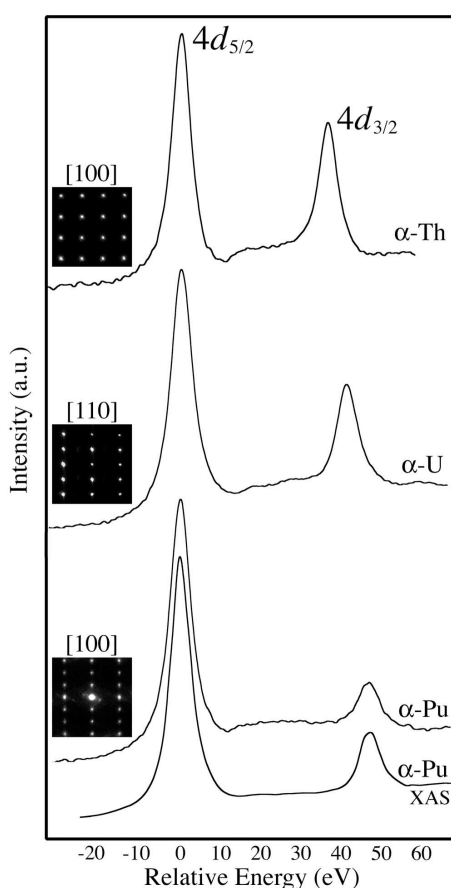


Figure 7

The  $N_{4,5}$  ( $4d \rightarrow 5f$ ) peaks from Th, U and Pu acquired by EELS in a TEM and from Pu acquired by XAS. A single crystalline diffraction pattern from each metal is presented, confirming the phase being examined by EELS.

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As another example of VSS experiments utilizing light sources, I would like to describe the recent work of J. Wong, et al [11] that led to a revolutionary measurement of the phonon dispersion curve (PDC) of fcc Pu-Ga (0.6 wt%) in the summer of 2003. The PDC is widely held to be the best measure of the interatomic potential and is used to judge the accuracy of calculated interatomic potentials. The very high quality data was obtained by this group at another light source, ESRF in Grenoble, France, a site chosen because the beam line properties of energy, flux and beam size (30 x 60 micrometers) were optimal. The VSS's, sealed in the experimental holder and packed in a shipping container, were safely transported across two continents and the Atlantic Ocean. The sample itself, 2.8 mm diameter and 10 micrometers thick, had been grown with unusually large grains so that the beam footprint could be situated within a single grain. This process led to single-crystal quality data. As in other examples presented in this section, this data showed features against which calculated interatomic potentials could be measured. In Fig. 8, the data shows: (a) the effect of high elastic anisotropy; (b) a Kohn anomaly, where electron-phonon coupling is pronounced; and (c) pronounced T[111] softening indicating the origins of the lattice instability active in the delta-to-alpha phase transition.

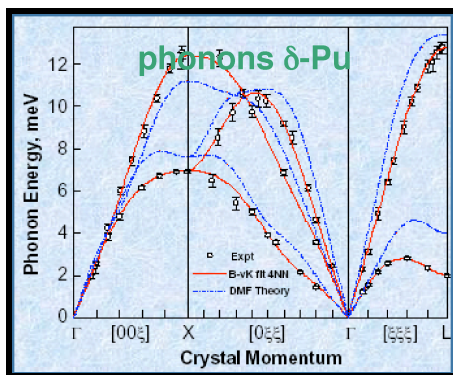


Figure 8  
Phonon dispersion of fcc Pu(Ga).  
Taken from Ref. 11

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### **New experimental techniques for VSS Pu samples using other facilities**

One of the most useful techniques for VSS experimentation is the TEM. It is used in many ways, both as a static characterization tool and, outfitted with various probes, as an experimental platform, as described in the examples above. Now, LLNL is developing an ultra-fast Dynamic TEM to understand the evolution of materials under stress in real time. [12]

Figure 9

Researchers at LLNL are developing a dynamic transmission electron microscope to study complex, transient events with unprecedented spatial and temporal resolution.





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But beyond TEM, other techniques are being developed to use in the lab. For example, in a recent talk at the Workshop on Fundamental Properties of Plutonium, held at VNIIEF, Sarov, 30 August to 3 September, 2004, I described the experiments of D. Jackson et al. [13] This group is using the designer DAC to measure the electrical resistance of Uranium. Their preliminary data showed the resistance falling with pressure up to 60 GPa, and rising as a function of temperature. Good agreement with earlier data was obtained at low temperatures. Currently, they are working to extend the pressure to 100 GPa.

In a final example, J. Crowhurst et al [14,15] have developed a DAC technique that utilizes laser-induced surface waves to measure the elastic constants of materials in the lab. This technique, impulsive stimulated light scattering (ISLS), has recently been applied to polycrystalline hcp  $\alpha$ -iron, and the shear and compressional elastic constants and sound velocities have been measured to 115 GPa. There is good agreement with other techniques at pressures where such data is available. This technique will undoubtedly be applied to Pu in the future.

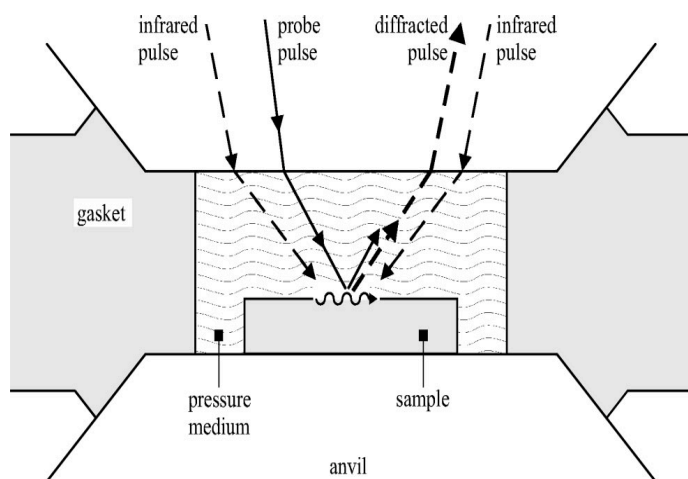


Figure 10

Schematic of cell cavity showing sample orientation and scattering configuration. [14]

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### **Summary**

VSS experiments are revealing the underlying physical properties that make plutonium an exceptional material. They are already yielding data that range from equation of state and electronic structure, to very accurate phonon dispersion curves. In the future we expect to see these experiments yielding accurate transport phenomena, and extending very accurate measurements of shear and compressional elastic constants to well above 100 Gpa.

This rich scientific benefit comes with practical benefits as well. VSS experiments are significantly less hazardous and more secure than traditional experiments. These properties result in substantial cost savings on a per-experiment basis.

Finally, VSS techniques applied to Pu are not isolated from other efforts. They provide a means to obtain data that cannot be obtained otherwise in a specific part of phase space and, at this stage of development, often rely on traditional experiments to validate their results in overlap regions. They also rely on successful applications of VSS techniques to other materials for validation of the technique itself. However, it is reasonable to expect that they will play an important role in the mosaic of experiments and theory that will comprise plutonium science in the future.

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